PROTOCOL FOR COLLECTION OF NUTRIENT GRAB SAMPLES

By

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Introduction

Since 2001, the Arcata Fish and Wildlife Office has been conducting water quality investigations in the Klamath River basin. One component of the investigations has been to collect water samples (grab samples) to identify levels of select nutrients, chlorophyll-a, and other constituents. This document is intended to provide field staff and users of the data generated from these investigations an understanding of the protocols and quality control measures instituted by the AFWO monitoring program.

Methods

Sample Collections in the Field

Upon arrival at each site, a 14 L sampling churn will be rinsed three times with deionized (D.I.) water. The goal of rinsing is equipment decontamination, the removal of substances adhering to equipment from previous exposure to environmental and other media (USGS Open File Report 00213). To do this, take 1/3 of a gallon of DI water and pour it in the churn, being careful never to touch any of the inside components of the churn. Next, shake the churn vigorously to assure that DI water contacts all interior surfaces, operate the plunger a few time, drain some water from the churn using the spigot and drain the rest through the lid. Repeat this process two more times using the remaining 2/3 of a gallon of DI water.

Bring the rinsed churn, Hydrolab Quanta (handheld multimeter) and all other necessary equipment down to the sample site. Set the barometric pressure on the Quanta and place it carefully upstream of the collection site. Ideally, the Quanta is placed on top of the housing for the DataSonde that is located at each site. This provides for the Quanta to be as close to the DataSonde as possible and keeps the Quanta sensors off the substrate, reducing the chance of bias from the sediment. This ensures that when you wade out to collect your sample, you do not disturb sediments that affect its readings. Sampling is generally done by wading from the bank as far as is safe. Be sure to be in water that is representative of the stream and is not affected by upstream tributaries or other activity upstream. The churn then is rinsed three times with stream water in the same procedure as before with the intent of ultimately filling the churn with water representative of the river at that location When rinsing and sampling, be sure to stand downstream of the churn making sure not to stir up the substrate where it would affect the sample. When the sample is to be collected, the churn is fully submerged into the stream then the lid is opened slightly to allow water from under the surface to enter. When it has filled, replace the lid and lift the churn from the water. The Quanta should be recorded once it has stabilized

and the churn has been filled with sample water. Record these values along with any information regarding stream and/ or weather conditions before filling bottles from the churn.

Churn Operation

Proper use of the churn guarantees the water is well mixed before the sample is collected. The churn should be stirred at a uniform rate by raising or lowering the splitter at approximately 9 inches per second (Bel-Art Products, 1993). This mixing must continue while the bottles are being filled. If filling is stopped for some reason, the stirring rate must be resumed before the next sample is drawn from the churn. As the volume of water in the churn decreases, the plunger round trip frequency increases as the velocity of the churn splitter remains the same. Care must be taken to avoid entraining air into the sample water as the splitter rises toward the top of the water in the churn. The churn does not reliably produce representative samples when it contains less than 4 liters of water, therefore if the water level reaches 4 liters or less, stop filling bottles and refill the churn from the stream. Completely filling the churn generally allows for all samples to be filled from one churn, which is preferred. If an unusually large number of samples will be drawn at a site and requires a refill of the churn, you should use good judgment as to which bottle sets should be sampled from each fill. Where quality control samples will be taken it is recommended that similar analyte groups be drawn from the same churn (e.g., regular and duplicate nitrate samples should be drawn from the same churn).

Sample Bottles

Sample bottles with and without chemical preservatives were provided by associated laboratories. In the case of bottles that contained chemical preservatives, bottles were not rinsed before sample collection and care was taken to avoid over-spillage that would result in chemical preservative loss. Sample bottles without chemical preservatives were rinsed with stream water from the churn 2-3 times before filling with sample water. Collected samples were placed in the dark in coolers on ice for transport to contracted laboratories for analysis.

Chain of Custody

Chain of Custody (COC) forms are filled out by a secondary crew member or after sampling takes place**.** Chain of Custody is a legal term that refers to the ability to guarantee the identity and integrity of the sample from collection through to reporting of the test results. A secure chain of custody, together with the analytical techniques used by the laboratory confirms the concentration of the sample present in the water, leading to the production of a legally defensible report**.** Be sure to fill in all information completely, including the date and time that the churn was collected, who collected the sample and if any changes were made to the analytes collected. The COC is used whenever a change in custody occurs.

<u>QA/QC – Duplicate, Spike and Blank bottle sets</u>

To ensure laboratory and sampling accuracy, one site every sampling period is selected to receive three additional QA/QC bottle sets. These bottle sets incorporate duplicate, blank and spiked water samples. Duplicate samples are collected the same way as regular samples and are used to assure the laboratory maintains precision within results.

Blank sample bottles are utilized to assess accuracy of the analysis and verify that the sampling method or laboratory equipment does not influence the results. After collection of all other samples at the QA/QC site, the churn is rinsed appropriately three times with D.I. water

before being filled with D.I. water. The blank bottle sets are collected in the same way as other samples, except using D.I. water in place of stream water. Blank samples are collected after all stream water samples are taken and act as a final rinse to decontaminate the churn.

A limited bottle set containing 'spiked' samples is also collected. Spike concentrations are determined based on past findings for each analyte. The spikes should be between 5 and 50 times the minimum detection limit or between 1 and 10 times the ambient level, whichever is greater (Eaton *et. al*., 1995). Known concentrations of selected analytes are generally added directly to the bottle in place of sample water to provide a sample with known levels of the specified analyte. Some situations have a known quantity and concentration of spike solution added to a known quantity of sample water submitted to the laboratory. The laboratory result then is calculated to find the expected stream concentration and compared to the original and duplicate values. Data forms containing the known spike concentrations are kept to verify that the lab is attaining accurate results.

Previous seasons (2001 and 2002) included filtered samples of some analytes. Filtered samples provided data to compare the dissolved vs. particulate fraction. Methods included operating a peristaltic pump with a cordless drill with a new hose inserted into the spigot of the churn. A disposable 45 micron filter cartridge provided for filtration to take place at each site.

All bottle sets are immediately placed on ice and are transported to the associated laboratories. This maintains the samples in the dark and as close to 4 ºC as possible. When necessary, dry ice is used for preserving samples. All grab samples were processed within 24 hours or within known laboratory holding periods. Any sample that was not processed within known hold times is reported within the case narrative sent by the analyzing laboratory.

Turbidity Samples

Turbidity samples are drawn directly from the flowing stream. The appropriately labeled turbidity bottle should be rinsed with stream water three times before taking the sample. Once the bottle has been rinsed, it is submerged and allowed to fill to the top, excluding air bubbles. Care should be taken to avoid the collection of surface water in the bottle. Once the bottle is filled, it is capped and placed into a cooler with ice along with the other water samples. Turbidity samples are analyzed at the Arcata Fish and Wildlife Office using a LaMotte 2020 turbidimeter within 24 hours of collection.

Sampling Instructions for Coliform Bacteria (North Coast Laboratories, 2004)

The container used for bacteria testing is sterile. Do not open the sample bottle until you are ready to collect your sample. Do not remove the preservative powder that is in the bottle.

Sampling from a well or stream**:**

1 Wash your hands
2 Remove the paperwork from around the sample container.
3 If possible, avoid sampling near river banks.
4 Unscrew the cap from the bottle and put the cap down with the open side facing up. DO NOT touch the inside of the cap or bottle.
5 Grasp the bottle at the base with one hand, position the bottle mouth slightly upward toward the current. Trying to avoid surface scum, plunge the bottle down into the water.

6 Be sure to fill the bottle to the 100 mL mark or above. Avoid over filling the bottle.

7 Replace the cap tightly. Keep your sample cold. It is important that your sample remain cold when transporting the sample to the laboratory. Do not put your sample in direct sunlight or near your car heater.

8 Fill out the information slip that was wrapped around your sample container. Be sure and include your name, address and phone number. The date and time that you collected your sample MUST be listed on the appropriate line. Someone at the laboratory will help with the analysis selection if you are unsure of the one you need.

9 Bring your sample to the laboratory as quickly as possible. All tests need to be started within 24 hours; some tests need to be started within 6 hours.

Bibliography

Bel-Art Products. 1993. Churn Sample Splitter Instructions, 37805 Series. Pequannock, NJ.

Eaton, Andrew D., Lenore S. Clesceri, and Arnold E. Greenberg., ed. 1995. Standard Methods for the Examination of Water and Wastewater. 19th Edition. Washington D.C.

Lurry,D.L. and C.M. Kolbe. 2000. Interagency field manual for the collection of Water Quality Data. USGS Publication, Open File Report 00-213.

North Coast Laboratories. 2004. Sampling Instructions for Coliform Bacteria. Arcata, CA.

Regional Laboratory for Toxicology. Chain of Custody. Updated Dec. 7, 2004, accessed 2/25/2005. http://www.toxlab.co.uk/coc.htm.